

PATENT SPECIFICATION

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(54) A PROCESS FOR REFINING GLYCERIDE OILS OR FATS

(71) We, ASAHI DENKA KOGYO KABUSHIKI KAISHA, a Japanese Company, of 7-1, Higashiogu, Arakawa-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for refining glyceride oils or fats, more particularly to a physical refining process in which free fatty acids are removed from the oils or fats by steam distillation by introducing the steam as a carrier gas under reduced pressure. Crude oils and fats usually contain free fatty acids, most of which are supposed to be formed by hydrolysis of the triglycerides under the influence of moisture, lipase and other catalytic materials in the course of the crushing or extracting process and during the storage period of the crude oils and fats. It is necessary for the production of refined oils and fats to remove the free fatty acids, although the free fatty acids content depends primarily on the quality of the crude oils and fats. The usual neutralization with alkali using caustic soda has, so far, been the common method for removing the free fatty acids (or deacidification). The alkali refining process has an advantage in that a variety of impurities and foreign matter in the crude oils and fats, such as pigments, proteins, phosphatides and metals, are supposed to be adsorbed by, and removed easily with, the fatty acid soaps produced in the oils and fats during alkali neutralization. As a result, refined oils and fats produced have a light colour, favourable flavour and good oxidation stability. However, the fatty acid soaps mentioned above adsorb considerable amount of neutral oil and also it is difficult to prevent the saponification of glycerides by alkali, and therefore a considerable loss of neutral oil has been pointed out as a serious disadvantage in the alkali deacidification process. Furthermore, a large quantity of washing water is necessary to remove the residual alkali and soaps in oils and fats, and the waste water so produced has high B.O.D. (biological oxygen demand) and C.O.D. (chemical oxygen

demand) values since it contains various materials. The waste water is unlikely to meet the regulations concerning water pollution without treatment involving considerable expense.

The soap stock obtained in the alkali refining process contains a large quantity of impurity. Therefore, acid oil which is produced by decomposing the soap stock with sulphuric acid is of poor quality. A physical refining process was proposed by E. Wecker and afterwards some modifications to it have also been performed. In accordance with these physical refining processes, however, deacidification and deodorization are carried out simultaneously in the same batch and thereby the refined oils and fats have inferior stability and colour as compared with that of alkali refining processes. It is an object of the present invention to provide an improved physical refining process which gives refined oils and fats of good quality in colour, flavour and oxidation stability.

The refining process of the present invention comprises contacting the glyceride oils or fats with acid, contacting the oils or fats with neutralizing agent to neutralize the acid, separating insoluble materials from the oils or fats, continuously introducing steam into the oils or fats to remove free fatty acids by distillation with the introduced steam, contacting the oils or fats with adsorbent as herein-after defined, separating the adsorbent and other insoluble materials from the oils or fats and deodorizing the oils or fats.

An embodiment of the refining process of the present invention is as follows. The crude oils or fats are firstly subjected to the acid treatment. The acid treatment is performed by adding the acid to the crude oils or fats in the amount of 0.05 to 1.0%, preferably 0.05 to 0.4% by weight of the oils or fats and mixing them for 2 to 15 minutes, preferably 5 to 10 minutes at a temperature of 45° to 85° C., preferably 55° to 75° C. under a reduced pressure or atmospheric pressure, preferably a reduced pressure of 5 to 20 mm Hg. The acids used in the step of acid treatment are the mineral acids such as sulphuric acid, hydrochloric acid and phosphoric acid and/or the

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organic acids such as acetic acid, oxalic acid and citric acid; preferably phosphoric acid. Thus the crude oils or fats are treated with acid and the acid treatment has the effect of making so-called gums and mucilaginous materials, which are supposed to comprise phosphatides, resins and proteins, insoluble and aggregative in form, so that they can be removed easily from the oils or fats. The oils or fats contacted with acid are subjected to treatment with a neutralizing agent to neutralize the added acid. The treatment with a neutralizing agent is performed by adding hydroxide and/or a basic salt of an alkali metal and/or an alkaline earth metal, such as sodium carbonate, sodium bicarbonate, calcium hydroxide, calcium carbonate and sodium hydroxide to the oils or fats which have been contacted with acid in an amount of 1 to 3, preferably, 1 to 2 equivalents of the acid used in the step of acid treatment, and mixing them. It is preferable to perform the neutralization of the acid by mixing the oils or fats with neutralizing agent for 5 to 30 minutes at a temperature of 45° to 85° C. under a reduced pressure of 5 to 20 mm Hg and using the carbonate and/or the bicarbonate, especially calcium carbonate as neutralizing agent. The acid added in the step of the acid treatment can be removed almost completely by contacting the oils or fats with neutralizing agent and consequently the oils or fats can be deacidified by treating at high temperature without being spoiled since they are deacidified in the absence of acid. Therefore, it is possible to obtain refined oils and fats of good quality. After the neutralization, the insoluble materials are separated from the oils or fats. However, it is preferable to add a filter aid to the oils or fats and mix them before separating the insoluble materials from the oils or fats. The filter aids used for this purpose are diatomaceous earth, activated clay, neutral clay, aluminosilicate, "celite" (Trade Mark) and activated carbon, preferably activated clay, diatomaceous earth and celite. When a filter aid is added to the oils or fats, it is preferable to add the filter aid to the oils or fats and mix at a temperature of 65° to 110° C., preferably 70° to 90° C. under reduced pressure or atmospheric pressure, especially reduced pressure of 5 to 20 mm Hg for 5 to 40 minutes, especially 10 to 30 minutes. Although the amount of filter aid depends on the kind of filter aid used, the preferable amount is 0.5 to 1.0% by weight of the oils or fats when activated clay, celite and diatomaceous earth are used as the filter aids. After the oils or fats have been neutralized and preferably thereafter contacted with the filter aid, such materials as the residual neutralizing agent, the produced salt, the filter aid and other insoluble materials are separated by filtration or press filtration or centrifugal separation and thereafter the oils or fats are subjected to a deacidification treatment to remove free fatty acids from the oils or fats. The deacidification treatment is performed by introducing steam continuously into the oils or fats at a temperature of 180° to 260° C., preferably 220 to 250° C. under a reduced pressure of 0.5 to 5 mm Hg, preferably 1 to 3 mm Hg and distilling off the free fatty acids with the introduced steam. Thus the free fatty acids are removed from the oils or fats by the steam distillation and also the heat decomposable materials in the oils or fats are decomposed, the heat denaturable materials in the oils or fats are denatured and the odoriferous components in the oils or fats are removed during the steam distillation. Therefore, the steam distillation contributes towards making the following steps of contacting with adsorbent and deodorizing more effective in refining the oils or fats. The adsorbent is one which will adsorb the products of the decomposition and denaturing. The oils or fats which have been deacidified by steam distillation are then subjected to adsorbent treatment. The adsorbent treatment is performed by adding the adsorbent such as activated carbon, alumina, silica, aluminosilicate, activated clay or natural clay to the oils or fats and mixing them for 10 to 40 minutes, preferably 20 to 30 minutes at a temperature of 65° to 150° C., preferably 90° to 115° C. under a reduced pressure or atmospheric pressure, preferably a reduced pressure of 5 to 50 mm Hg. It is preferable to use an adsorbent which is an efficient filter aid as well as an efficient adsorbent, especially activated clay. Although the amount of the adsorbent used in the above-mentioned treatment is dependent on the kind of adsorbent used, the preferred amount of the adsorbent is 2 to 4% by weight of the oils or fats, when activated clay is used as the adsorbent. After contacting the oils and fats with the adsorbent, the adsorbent, the adsorbed materials and also the insoluble materials are separated from the oils or fats by filtration or press filtration or centrifugal separation and thereafter the oils or fats are subjected to the deodorization step. The deodorization is performed by continuously introducing steam into the oils or fats at a temperature of 180° to 270° C., preferably 230° to 260° C. under a reduced pressure of 0.5 to 6 mm Hg, preferably 2 to 4 mm Hg and removing the odoriferous materials with the steam from the oils and fats. Although the refining process of this invention is applicable to vegetable oils such as palm oil, palm kernel oil, coconut oil, babassu oil, olive oil, almond oil and rapeseed oil and animal fats such as tallow and lard, the refining process of this invention is more effective in refining the vegetable oils such as palm oil, palm kernel oil, coconut oil, babassu oil and olive oil, especially palm oil. The method

separation and thereafter the oils or fats are subjected to a deacidification treatment to remove free fatty acids from the oils or fats.

The deacidification treatment is performed by introducing steam continuously into the oils or fats at a temperature of 180° to 260° C., preferably 220 to 250° C. under a reduced pressure of 0.5 to 5 mm Hg, preferably 1 to 3 mm Hg and distilling off the free fatty acids with the introduced steam.

Thus the free fatty acids are removed from the oils or fats by the steam distillation and also the heat decomposable materials in the oils or fats are decomposed, the heat denaturable materials in the oils or fats are denatured and the odoriferous components in the oils or fats are removed during the steam distillation.

Therefore, the steam distillation contributes towards making the following steps of contacting with adsorbent and deodorizing more effective in refining the oils or fats. The adsorbent is one which will adsorb the products of the decomposition and denaturing.

The oils or fats which have been deacidified by steam distillation are then subjected to adsorbent treatment. The adsorbent treatment is performed by adding the adsorbent such as activated carbon, alumina, silica, aluminosilicate, activated clay or natural clay to the oils or fats and mixing them for 10 to 40 minutes, preferably 20 to 30 minutes at a temperature of 65° to 150° C., preferably 90° to 115° C. under a reduced pressure or atmospheric pressure, preferably a reduced pressure of 5 to 50 mm Hg. It is preferable to use an adsorbent which is an efficient filter aid as well as an efficient adsorbent, especially activated clay.

Although the amount of the adsorbent used in the above-mentioned treatment is dependent on the kind of adsorbent used, the preferred amount of the adsorbent is 2 to 4% by weight of the oils or fats, when activated clay is used as the adsorbent. After contacting the oils and fats with the adsorbent, the adsorbent, the adsorbed materials and also the insoluble materials are separated from the oils or fats by filtration or press filtration or centrifugal separation and thereafter the oils or fats are subjected to the deodorization step.

The deodorization is performed by continuously introducing steam into the oils or fats at a temperature of 180° to 270° C., preferably 230° to 260° C. under a reduced pressure of 0.5 to 6 mm Hg, preferably 2 to 4 mm Hg and removing the odoriferous materials with the steam from the oils and fats.

Although the refining process of this invention is applicable to vegetable oils such as palm oil, palm kernel oil, coconut oil, babassu oil, olive oil, almond oil and rapeseed oil and animal fats such as tallow and lard, the refining process of this invention is more effective in refining the vegetable oils such as palm oil, palm kernel oil, coconut oil, babassu oil and olive oil, especially palm oil. The method

of this invention provides refined oils or fats of better colour, taste, stability and other qualities than the methods of refining by steam distillation or deacidification which have been disclosed so far and also provides distilled and recovered free fatty acids of good quality which contain only small quantities of impurities.

The following examples illustrate this invention. However, this invention is not limited to the following examples.

Example 1.

Crude palm oil (acid value 6.46) was subjected to acid treatment which was carried out by adding 75% ortho-phosphoric acid to the oil in an amount of 0.2% by weight of the oil and mixing at 65° C. under reduced pressure of 10 to 20 mmHg for 10 minutes. The acid treated oil was subjected to neutralization which was carried out by adding calcium carbonate to the oil in an amount of 0.3% by weight of the oil and stirring the oil at 65° C. under a reduced pressure of 10 to 20 mm Hg for 10 minutes. Thereafter, activated clay was added to the oil, as a filter aid, in an amount of 0.5% by weight of the oil and mixed with the oil at 75° C. under a reduced pressure of 10 to 20 mm Hg for 20 minutes. The palm oil was then filtered with suction to remove the filter aid and other insoluble materials. After filtration, the palm oil was subjected to deacidification which was carried out by introducing steam continuously into the oil at 230° C. under a reduced pressure of 2 mm Hg for 30 minutes. Then the oil was cooled to 80° C. and the pressure was restored to atmospheric pressure by introducing nitrogen gas. The oil obtained had an acid value of 0.05. The oil was subjected to an adsorbent treatment which was carried out by adding activated clay to the oil in an amount of 2.5% by weight of the oil and stirring at 110° C. under a reduced pressure of 10 to 20 mm Hg for 20 minutes. After cooling the oil to a temperature of 80° C., the oil was filtered with suction to remove the adsorbent and other materials. The filtered oil had the colour red 0.5 and yellow 4.0 using a 2 inch cell in a Lovibond Tintometer. The oil was then subjected to deodorization which was carried out by introducing steam at a temperature of 250° C. under a reduced pressure of 2 mm Hg for 1 hour. The refined oil had the colour red 0.4 and yellow 2.7 using the 2 inch cell in the Lovibond Tintometer "Lovibond" is a Trade Mark) and also had good flavour and good stability as shown in Table 1 and Table 2.

Example 2.

Crude palm oil (acid value 6.46) which was the same oil as in Example 1 was subjected to acid treatment which was performed by adding 75% ortho-phosphoric acid to the oil in an amount of 0.2% by weight of the oil

and stirring for 10 minutes at 65° C. under a reduced pressure of 10 to 20 mm Hg. Then the oil was neutralized by adding calcium carbonate to the oil in an amount of 0.4% by weight of the oil and stirring for 10 minutes at 65° C. under a reduced pressure of 10 to 20 mm Hg. Celite was then added to the oil in an amount of 0.5% by weight of the oil and the oil stirred for 10 minutes at 80° C. under a reduced pressure of 10 to 20 mm Hg. Thereafter, the oil was filtered with suction to remove celite, residual neutralizing agents, salt and other insoluble materials. The filtered oil was then subjected to steam deacidification which was carried out by the same procedure as in Example 1. The deacidified oil had an acid value of 0.08. The acidified oil was subjected to an adsorbent treatment which was carried out by adding activated clay to the oil in an amount of 3% by weight of the oil and then stirring under the same conditions as in Example 1 and the oil was then filtered with suction. The oil obtained had the colour red 0.5 and yellow 6.1 using a 2 inch cell in a Lovibond Tintometer. The oil was then subjected to deodorization which was carried out by the same procedure as in Example 1. The refined oil had the colour red 0.4 and yellow 3.2 using the 2 inch cell in the Lovibond Tintometer and also had good flavour and good stability as shown in Table 1 and Table 2.

Example 3.

Crude palm oil (acid value 6.46) which was the same oil as in Example 1 was subjected to acid treatment which was carried out by the same procedure as in Example 1 and then treated with calcium carbonate by the same procedure as in Example 1 and then filtered with suction to remove the insoluble materials. Thereafter, the oil was subjected to deacidification which was carried out by the same procedure as in Example 1. The deacidified oil had an acid value of 0.06. The deacidified oil was then subjected to an adsorbent treatment which was carried out by adding activated clay to the oil in an amount of 3% by weight of the oil and stirring under the same condition as in Example 1. The oil was then filtered with suction to remove the activated clay and other materials. The obtained oil had the colour red 0.4 and yellow 5.9 using a 2 inch cell in a Lovibond Tintometer. The oil was then subjected to deodorization which was carried out by the same procedure as in Example 1. The deodorised oil had the colour red 0.3 and yellow 3.8 using the 2 inch cell in the Lovibond Tintometer and also had good flavour and good stability as shown in Table 1 and Table 2.

Example 4.

Crude palm oil (acid value 4.68) was treated with orthophosphoric acid and then neutralized with calcium carbonate and treated with the

activated clay and then filtered with suction, and deacidified by steam distillation by the same procedures as in Example 1. The obtained oil had an acid value of 0.07. The oil obtained 5 was then subjected to an adsorbent treatment which was carried out by the same procedure as in Example 1. The oil was then filtered with suction to remove the adsorbent and other materials. The filtered oil had the colour red 10 0.4 and yellow 6.4 using a 2 inch cell in a Lovibond Tintometer. The filtered oil was then subjected to deodorization which was carried out by the same procedure as in Example 1. The deodorized oil had the colour red 0.3 15 and yellow 2.4 using the 2 inch cell in the Lovibond Tintometer and also had good flavour and good stability as shown in Table 1 and Table 2.

Example 5.

20 Coconut oil (acid value 11.04) was refined by the same procedure as in Example 1. The refined coconut oil had the colour red 0.2 and yellow 1.1 using a 2 inch cell in a Lovibond Tintometer.

Comparative Example 1.

Crude palm oil (acid value 6.46) was subjected to acid treatment which was carried out by adding 85% ortho-phosphoric acid to the oil in an amount of 0.05% by weight of the oil and stirring for 30 minutes at 50° C. 25 under 10 to 20 mm Hg. The acid treated oil was then subjected to an adsorbent treatment which was carried out by adding activated clay to the oil in an amount of 3% by weight of the oil and stirring for 30 minutes at 105° C. 30 under a reduced pressure of 10 to 20 mm Hg. Then the oil was filtered to remove the adsorbent and other materials. The filtered oil was subjected to steam distillation to deacidify and deodorize simultaneously which was carried out by continuously introducing steam into the oil at 270° C. under a reduced pressure of 5 mm Hg for 30 minutes. The refined oil had the colour red 1.0 and yellow 7.0 using a 2 35 inch cell in a Lovibond Tintometer and also had a residual odour of crude palm oil or an unfavourable odour. The results of an A.O.M. test and a heat stability test are shown in Table 1 and Table 2. 40

TABLE 1
The Results of the A.O.M. Test*

| Sample | Time (hours) |
|-----------------------------------|--------------|
| Refined oil obtained by Example 1 | 76 |
| by Example 2 | 74 |
| by Example 3 | 79 |
| by Example 4 | 81 |
| by Comparative Example 1 | 62 |

* The A.O.M. test was carried out by adding 300 ppm of tocopherol and 30 ppm of citric acid to the refined oils.

TABLE 2
The Results of the Heat Stability Test*

| Sample | Colour ** before the test | Flavour during heating | Colour ** after the test |
|---------------------------------------|------------------------------|---------------------------|-----------------------------|
| (Red/Yellow) | | | |
| The refined oil obtained by Example 1 | 0.4/2.7 | good | 0.8/5.3 |
| by Example 2 | 0.4/3.2 | good | 0.9/6.2 |
| by Example 3 | 0.3/3.8 | good | 0.8/5.5 |
| by Example 4 | 0.3/2.4 | good | 0.9/5.0 |
| by Comparative Example 1 | 1.0/7.0 | undesirable flavour | 2.0/20.0 |

* The heat stability test was carried out at 200°C. for 5 hours.

** The colour was determined using a 2 inch cell in a Lovibond Tintometer.

WHAT WE CLAIM IS:—

1. A process for refining glyceride oils or fats which comprises contacting the crude oils or fats with acid and then with neutralizing agent to neutralize the acid, separating insoluble materials from the oils or fats, introducing steam continuously into the oils or fats to remove free fatty acids, by distillation with the introduced steam, contacting the oils or fats with adsorbent as hereinbefore defined, separating the adsorbent and other insoluble materials from the oils or fats and deodorizing the oils or fats.
2. A process as claimed in claim 1, wherein contacting the oils or fats with acid is carried out by adding the acid to the oils or fats in an amount of 0.05 to 1.0% by weight of the oils or fats and mixing for 2 to 15 minutes at a
3. A process as claimed in claim 1 or claim 2 wherein contacting the oils or fats with neutralizing agent is carried out by adding neutralizing agent to the oils and fats in an amount of 1 to 3 equivalents of added acid and mixing for 5 to 30 minutes at a temperature of 45° to 85° C. under a reduced pressure of 5 to 20 mm Hg.
4. A process as claimed in any one of the preceding claims, wherein continuously introducing the steam into the oils or fats to remove free fatty acid is carried out at a temperature of 180° to 260° C. under a reduced pressure of 0.5 to 5 mm Hg.
5. A process as claimed in any one of the preceding claims, wherein contacting the oils

temperature of 45° to 85° C. under a reduced pressure of 5 to 20 mm Hg.

3. A process as claimed in claim 1 or claim 2 wherein contacting the oils or fats with neutralizing agent is carried out by adding neutralizing agent to the oils and fats in an amount of 1 to 3 equivalents of added acid and mixing for 5 to 30 minutes at a temperature of 45° to 85° C. under a reduced pressure of 5 to 20 mm Hg.

4. A process as claimed in any one of the preceding claims, wherein continuously introducing the steam into the oils or fats to remove free fatty acid is carried out at a temperature of 180° to 260° C. under a reduced pressure of 0.5 to 5 mm Hg.

5. A process as claimed in any one of the preceding claims, wherein contacting the oils

5 or fats with the adsorbent is carried out by adding the adsorbent to the oils or fats and mixing for 10 to 40 minutes at a temperature of 65° to 150° C. under a reduced pressure of 5 to 50 mm Hg. 25

10 6. A process as claimed in any one of the preceding claims, wherein deodorizing the oils or fats is carried out by introducing steam continuously into the oils or fats at the temperature of 180° to 270° C. under a reduced pressure of 0.5 to 6 mm Hg. 30

15 7. A process as claimed in any one of the preceding claims, wherein the acid is ortho-phosphoric acid. 35

20 8. A process as claimed in any one of the preceding claims, wherein the adsorbent is activated clay. 40

9. A process as claimed in any one of the preceding claims, wherein the neutralizing agent is calcium carbonate.

10. A process as claimed in any one of the preceding claims, wherein the oils or fats are contacted with a filter aid after contacting with neutralizing agent.

11. A process as claimed in claim 10, where- 25
in the oils or fats are contacted with the filter aid by adding the filter aid to the oils or fats at a temperature of 65° to 110° C. under a reduced pressure of 5 to 20 mm Hg for 5 to 40 minutes. 30

12. A process as claimed in claim 10 or claim 11, wherein the filter aid is selected from activated clay, celite, diatomaceous earth and mixtures thereof. 35

13. A process as claimed in claim 11, where- 35
in the amount of filter aid is 0.5 to 1.0% by weight of the oils or fats. 40

14. A process as claimed in any one of the preceding claims, wherein the oil or fat is a palm oil. 40

15. A process as claimed in claim 1 and substantially as hereinbefore described with reference to any one of Examples 1 to 5. 40

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